



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :  
G01J 3/06, G02B 26/08, G01J 3/30

A1

(11) International Publication Number: WO 96/34256

(43) International Publication Date: 31 October 1996 (31.10.96)

(21) International Application Number: PCT/GB96/00970

(22) International Filing Date: 24 April 1996 (24.04.96)

(30) Priority Data:  
9508343.2 25 April 1995 (25.04.95) GB

(71) Applicant (for all designated States except US): RENISHAW PLC [GB/GB]; New Mills, Wotton-under-Edge, Gloucestershire GL12 8JR (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): BATCHELDER, David, Neville [GB/GB]; 2A Foxhill Avenue, Leeds, Yorkshire LS16 5PB (GB).

(74) Agent: JACKSON, John, Timothy; Renishaw plc, Patent Dept., New Mills, Wotton-under-Edge, Gloucestershire GL12 8JR (GB).

(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

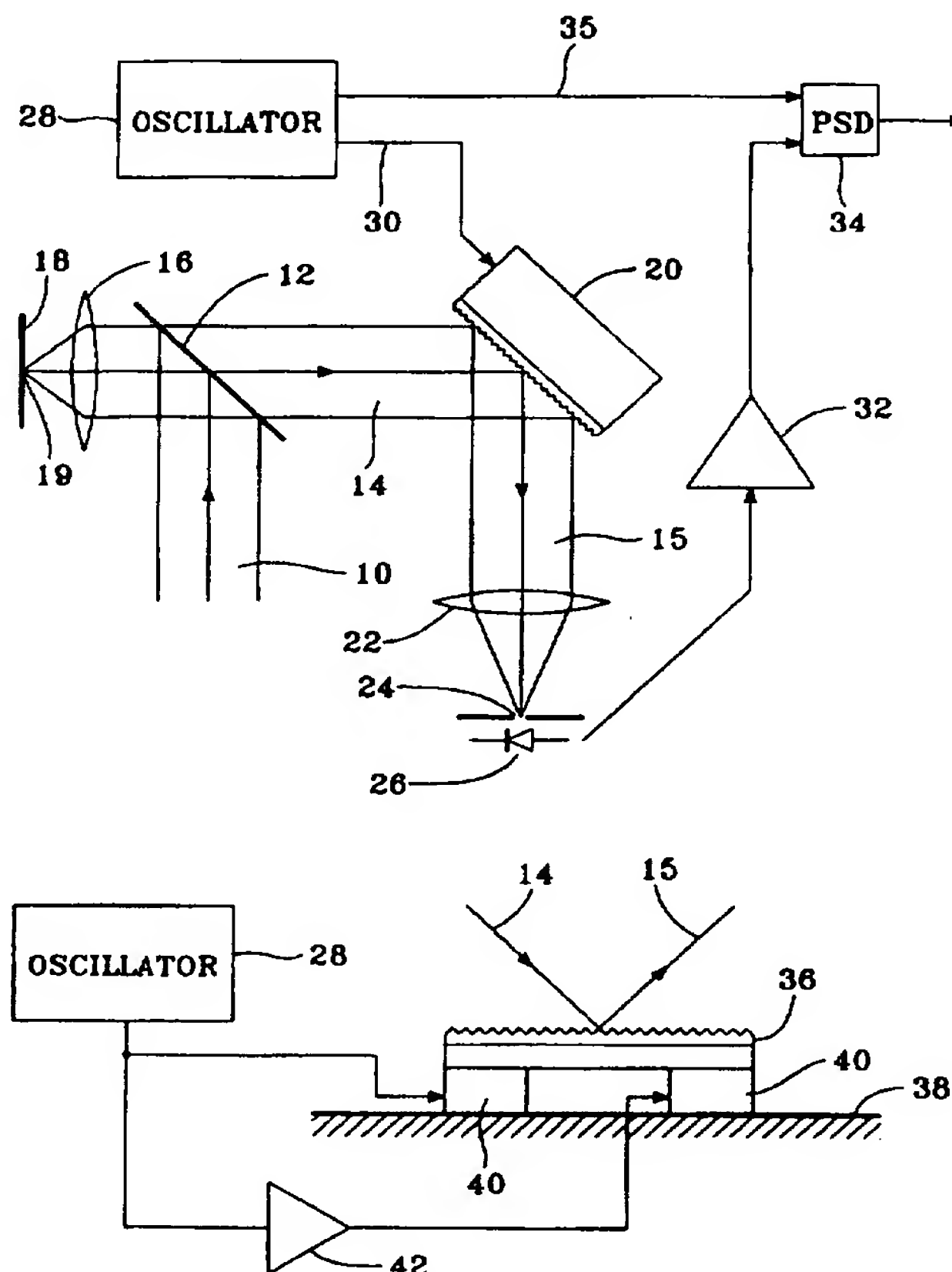
Published

With international search report.

(54) Title: SPECTROSCOPIC APPARATUS

(57) Abstract

A line in a Raman spectrum scattered from a sample (18) is selected by a diffraction grating (20) and passed to a detector (26). The grating (20) may be based on an electrostrictive device and has a variable pitch. It is tuned about the selected Raman line under the control of an oscillator (28). The output from the detector (26) is analysed synchronously with the oscillation by a phase sensitive detector (34). This rejects background light and enables, for example, confirmation of the existence of the Raman line in the spectrum, and measurement of its height above the background. The variable pitch grating (20) may be replaced by a fixed pitch grating or a tunable filter, mounted on an oscillatory drive which may comprise electrostrictive or piezoelectric elements.



***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**SPECTROSCOPIC APPARATUS**

This invention relates to spectroscopy.

5 Spectroscopic apparatus for analysing the Raman spectrum of a sample is disclosed in, for example, our European Patent Application No. EP 543578. A sample is illuminated by monochromatic laser light, and the resulting Raman scattered light is analysed, either by a diffraction  
10 grating which disperses the Raman spectrum, or by a non-dispersive tunable filter (e.g. an interference filter).

In one aspect, the present invention relates to spectroscopic apparatus having a diffraction grating for  
15 dispersing a spectrum, the diffraction grating having a variable pitch. In other aspects of the invention, the variable pitch diffraction grating may be replaced by a diffraction grating or filter which is tunable, for example by rotating it about an axis perpendicular to the optical  
20 axis.

Preferred embodiments of the invention will now be described by way of example, with reference to the accompanying drawings, wherein:

25

Fig 1 is a schematic diagram of a first Raman spectrometer, and

Fig 2 is a schematic diagram of part of a modified Raman  
30 spectrometer.

In Fig 1, an incoming laser beam 10 is reflected through 90° by a dichroic filter 12 placed at 45° to the optical path. It is focused by a lens 16 to a spot 19 on a sample  
35 18. Raman scattered light produced from the sample 18 as a result is collected by the lens 16 and passes back through the system. The Raman scattered light 14 is transmitted by the dichroic filter 12, while Rayleigh scattered light at

the same frequency as the incoming laser beam is rejected by this filter. The Raman scattered light 14 is incident upon a diffraction grating 20, which reflects a dispersed spectrum of the Raman light. Light 15 of one particular Raman peak of interest within this spectrum is focused by a lens 22 onto a slit 24, which may for example accept only  $20\text{cm}^{-1}$  of the dispersed spectrum. This slit 24 thus acts to select a particular Raman line of interest in the spectrum produced by the sample 18. The light passing through the slit 24 is detected by a suitable detector, such as an avalanche photodiode 26. Of course, the slit 24 may accept a narrower or wider band than  $20\text{cm}^{-1}$ , if desired.

Any desired Raman line of interest may be selected by rotating the diffraction grating 20 about an axis normal to the optical axis, so that the desired Raman line is focused on the slit 24.

The diffraction grating 20 has a variable pitch. It may be based upon an electrostrictive device, the grating pitch varying in accordance with a variable voltage applied to the electrostrictive device. In one example of such a device, the grating may be recorded holographically, e.g. in a gelatin film which is provided on an electrostrictive substrate. A suitable variable diffraction grating based upon an electrostrictive device has recently been proposed by Cookson Technology Centre, Sandy Lane, Yarnton, Kidlington, Oxfordshire, OX5 1PF, United Kingdom.

In the arrangement shown in Fig 1, the electrostrictive device in the grating 20 is driven from an oscillator 28, producing (for example) a sinusoidal output on a line 30. In response to this, the pitch of the grating 20 varies sinusoidally with time, e.g. by about 0.2%. This produces a corresponding variation in the wavenumber of the Raman light selected by the slit 24. Typically, the variation is sufficient to enable scanning between the point of maximum intensity on a desired Raman peak and a point just off the

peak where only background light is received, e.g. caused by thermal effects, fluorescence, etc.

- For best results, the output 30 of the oscillator 28 should consist of the desired oscillation, superimposed on a DC level. Otherwise, if the electrostrictive device is operated by a signal which alternates about zero, it will cause frequency doubling and harmonic distortion.
- 10 The output signal from the detector 26 is taken via signal conditioning circuitry 32 to a phase sensitive detector (PSD) 34. The PSD 34 also receives an output 35 from the oscillator 28, which is synchronous with the AC component on the output 30. The PSD 34 therefore produces an output
- 15 representing the scanned Raman peak, from which its intensity (height) may easily be determined. Noise and the DC component produced by the thermal background, fluorescence etc. are rejected by the PSD 34.
- 20 The apparatus described has a number of possible uses. It can be used in various process control applications. For example, it may be used to monitor the growth of a diamond film by chemical vapour deposition, the grating 20 and slit 24 being arranged to scan the characteristic Raman peak of
- 25 diamond at  $1332\text{cm}^{-1}$ . The apparatus is also useful in situations in which one is looking to see if a given Raman line appears, e.g. during chromatography. The technique described gives a null signal until the Raman line appears.
- 30 The apparatus described has the advantage that there are no mechanical moving parts.

Although it has been described in relation to Raman spectroscopy, the described apparatus and techniques can be

35 used to examine the lines produced in any other kind of spectroscopy. Furthermore, the apparatus can have various extra components or modifications, e.g. as suggested in our European application no. EP 543578. It is also possible to

provide separate laser illumination of the sample 18, rather than injecting the laser beam 10 via the filter 12.

Fig 2 shows a modified apparatus. Most of the apparatus is the same as Fig 1, and has therefore not been shown in Fig 2. However, in place of the variable pitch diffraction grating 20, a fixed pitch diffraction grating 36 is used. This is mounted onto a mounting plate 38 via an oscillatory drive comprising two electrostrictive devices 40. One of these electrostrictive devices 40 is driven directly from the oscillator 28, while the other is driven in anti-phase via an inverter 42. The result is to produce a rocking motion of the diffraction grating 36 relative to the mounting plate 38. The result is the same as in the apparatus of Fig 1: the part of the spectrum which is selected by the slit 24 can be made to scan a Raman line of interest at the frequency of the oscillator 28. Piezoelectric devices may be used in place of the electrostrictive devices 40, if desired. Other oscillatory drives can also be used, for example the grating 36 may be mounted on a rotary table which can be oscillated by a suitable motor.

In a further modification (not shown) a tunable narrow band filter (e.g. an interference filter) may be used in place of the diffraction grating 20 or 36. Such a filter is tuned by rotating it to a desired tilt angle about an axis which is normal to the optical axis. In the present case, a suitable rotary drive is used to oscillate the filter about this tilt axis, at the frequency of the oscillator 28.



**CLAIMS:**

1. Spectroscopic apparatus in which a spectrum of light is received from a sample and analysed, comprising:
  - 5 a detector;  
means for selecting a line from said spectrum and passing it to the detector, said selecting means being tunable at least about said line in response to an input signal;
  - 10 an oscillator connected to the selecting means to provide said input signal, whereby the selecting means oscillates about said line and passes the resulting light to the detector; and  
a signal processing circuit connected to the detector  
15 to analyse said line.
2. Spectroscopic apparatus according to claim 1, in which the signal processing circuit comprises a phase sensitive detector which is also connected to the oscillator, whereby  
20 said line is analysed synchronously with the oscillation of the selecting means about said line.
3. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a diffraction  
25 grating having a pitch which is variable in response to said input signal.
4. Spectroscopic apparatus according to claim 3, wherein the diffraction grating comprises an electrostrictive  
30 device.
5. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a diffraction grating, mounted on an oscillatory drive driven by the  
35 oscillator.

6. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a tunable filter, mounted on an oscillatory drive driven by the oscillator.
- 5 7. Spectroscopic apparatus according to claim 5 or claim 6, wherein the oscillatory drive comprises at least one electrostrictive or piezoelectric device for rocking the selecting means.
- 10 8. Spectroscopic apparatus in which a spectrum of light is received from a sample and analysed, comprising:  
a detector; and  
a diffraction grating for dispersing the spectrum and passing at least a line from said spectrum to the detector,  
15 said diffraction grating having a pitch which is variable in response to an input signal.
9. Spectroscopic apparatus according to claim 8, wherein the diffraction grating comprises an electrostrictive  
20 device.



1/1

Fig. 1

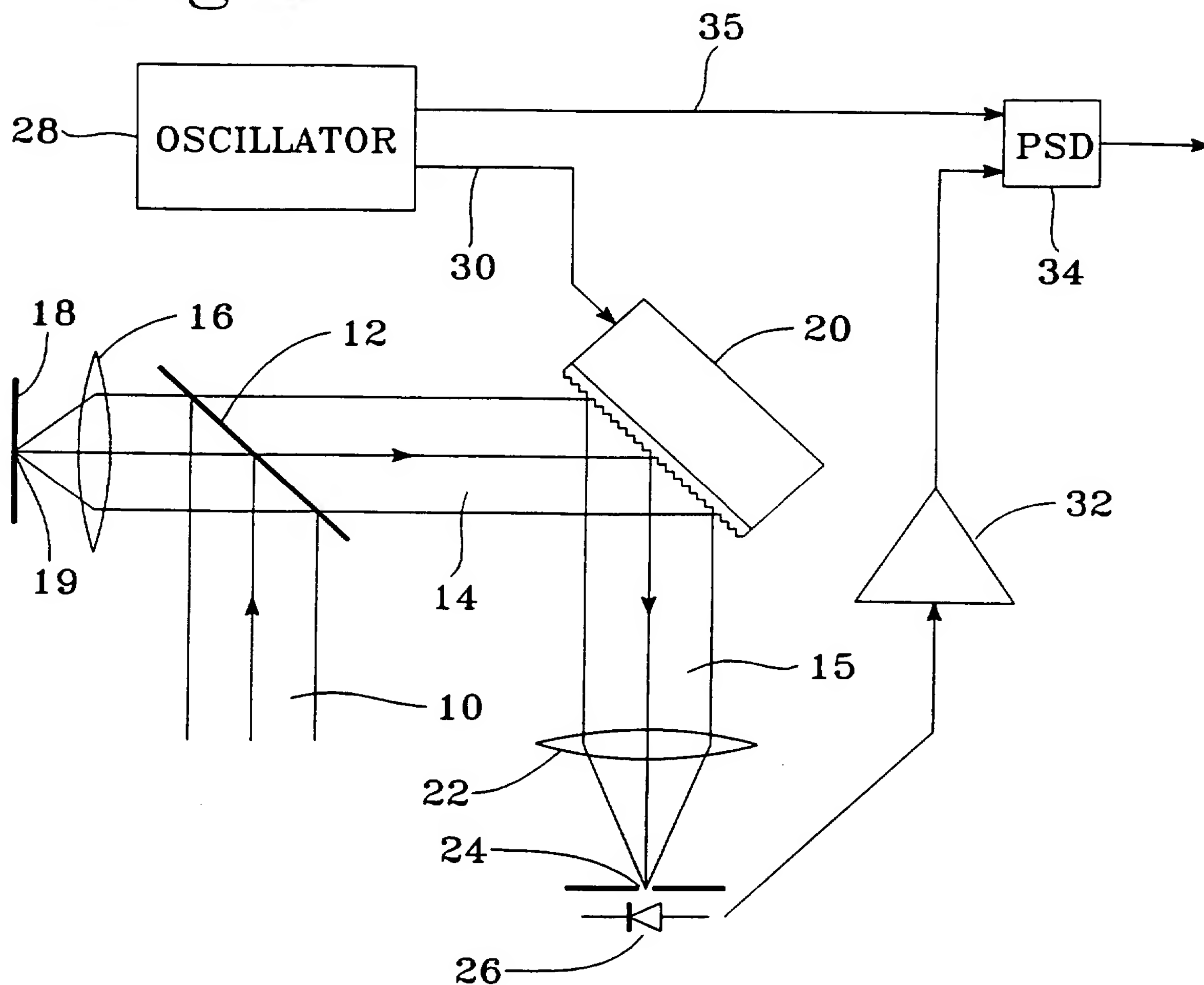
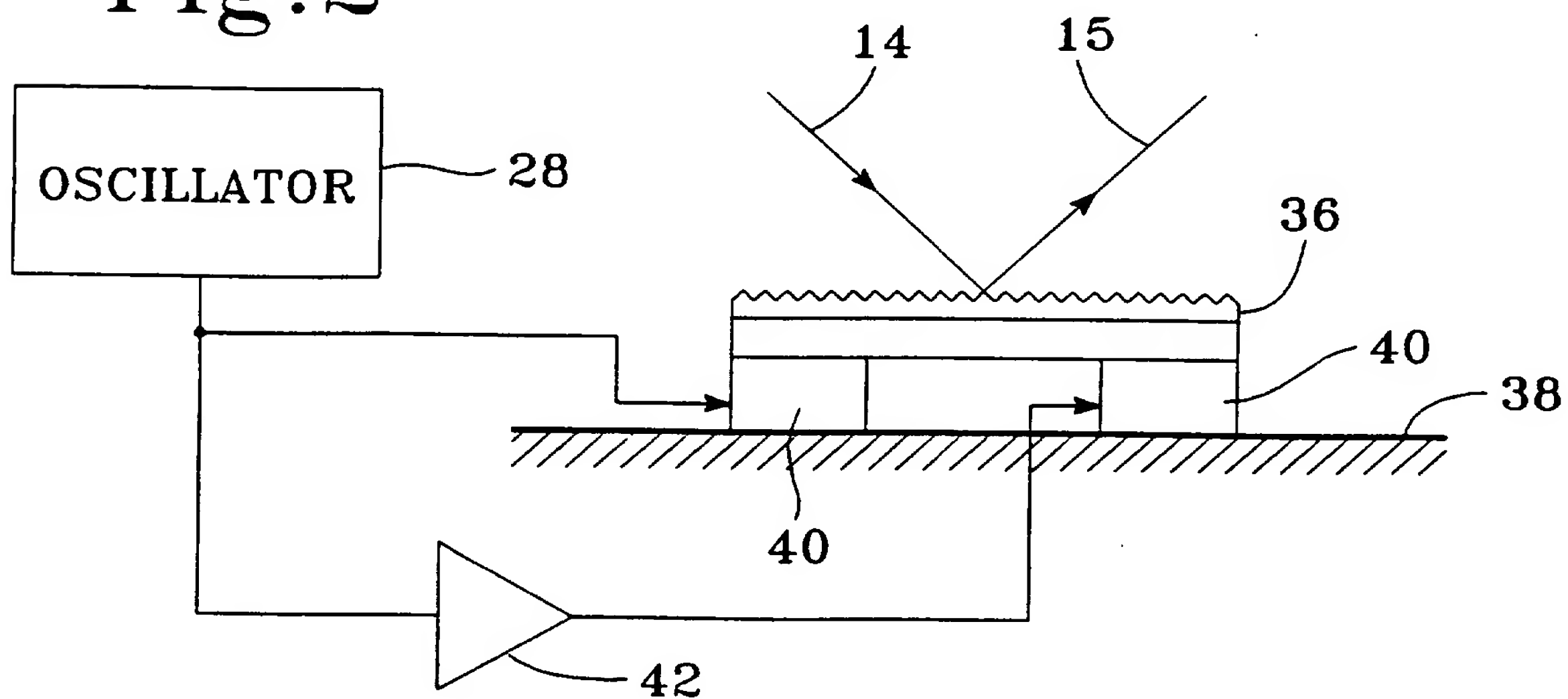


Fig. 2



# INTERNATIONAL SEARCH REPORT

In ☐ International Application No  
PCT/GB 96/00970

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G01J3/06 G02B26/08 G01J3/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G01J G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,39 43 387 (AKAD WISSENSCHAFTEN DDR) 5 July 1990	1-4,7-9
Y	see the whole document ---	5,6
Y	US,A,5 225 888 (SELWYN GARY S ET AL) 6 July 1993 see column 10; figures 5,6 ---	6
Y	EP,A,0 510 856 (SIEMENS PLESSEY CONTROLS LTD) 28 October 1992 see the whole document ---	6
Y	US,A,4 835 393 (KRAUSS LUTZ) 30 May 1989 see column 6, last paragraph see column 7, line 30 - line 44; figure 1 ---	5
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

30 July 1996

Date of mailing of the international search report

09.08.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Scheu, M

INTERNATIONAL SEARCH REPORT

In tional Application No  
PCT/GB 96/00970

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	US,A,5 504 576 (OHLE KLAUS-MICHAEL ET AL) 2 April 1996 see column 3, line 13 - line 40; figures ---	5
A	WOLFGANG DEMTRÖDER: "Laserspektroskopie, Grundlagen und Techniken" 1993 , SPRINGER , BERLIN XP002009680 see page 293 - page 294, paragraph 1 -----	2

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/GB 96/00970

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3943387	05-07-90	NONE	
-----			
US-A-5225888	06-07-93	JP-A- 4303745	27-10-92
		JP-B- 7092435	09-10-95
-----			
EP-A-0510856	28-10-92	CA-A- 2066816	27-10-92
		GB-A- 2255178	28-10-92
		JP-A- 6167448	14-06-94
		US-A- 5268745	07-12-93
-----			
US-A-4835393	30-05-89	DE-A- 3537482	06-11-86
		WO-A- 8702772	07-05-87
		EP-A- 0243375	04-11-87
		JP-T- 63500206	21-01-88
-----			
US-A-5504576	02-04-96	DE-A- 4214186	04-11-93
		WO-A- 9322636	11-11-93
		EP-A- 0638162	15-02-95
-----			